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(54) Title: INK JET INK FORMULATIONS CONTAINING MODIFIED CARBON PRODUCTS

(57) Abstract

There is disclosed an aqueous ink jet ink composition comprising an aqueous vehicle and a modified carbon product containing carbon having attached at least one organic group. The organic group comprises a) at least one aromatic group and b) at least one ionic group, at least one ionizable group, or a mixture of an ionic group and an ionizable group. The organic group having an aromatic group is directly attached to the carbon by the aromatic group. The organic group may comprise a) at least one C₁-C₁₂ alkyl group and b) at least one ionic group, at least one ionizable group, or a mixture of an ionic group and an ionizable group. Ink jet recording methods applying an ink jet ink of the present invention are also described.

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INK JET INK FORMULATIONS CONTAINING MODIFIED CARBON PRODUCTS

5 This application is a continuation-in-part of U.S. patent application serial nos. 08/356,460 and 08/356,653, both filed December 15, 1994, the disclosures of which are herein incorporated by reference.

BACKGROUND OF THE INVENTION

Field of the Invention

10 This invention relates to aqueous ink formulations for ink jet printing which contain carbon products as pigments.

Discussion of the Related Art

15 Ink jet printing is a non-impact process wherein droplets of ink are produced and deposited on a substrate such as paper, transparent film, or textile material in response to an electronic signal. Typical ink jet printing systems are continuous stream or drop-on-demand type. In continuous ink jet systems, ink is emitted in a continuous stream under pressure through at least one orifice or nozzle. The stream is perturbed causing it to break up into droplets at a fixed distance from the orifice. At the breakup point, the droplets are charged in accordance with digital data signals and passed through an electrostatic field. The field adjusts the trajectory of each droplet to direct it to a gutter for recirculation or to a specific location on a recording medium to create images. In drop-on-demand systems, a droplet is expelled from an orifice directly to a position on a recording medium by pressure generated in accordance with digital data signals. A droplet is not formed or expelled unless it is to be placed on the recording medium. The drop-on-demand system has several advantages over the continuous system in that it requires no ink recovery, charging, or deflection.

20 There are three basic types of drop-on-demand ink jet systems. One type has an ink filled channel with a nozzle on one end and a piezoelectric transducer near the other end which produces pressure pulses. The relatively large size of the transducer prevents close spacing of the nozzles, which may limit print quality. Physical limitations of the transducer result in low ink drop velocity and slow printing speed. The low drop velocity may also diminish tolerances for drop velocity variation and directionality.

25 A second type of drop-on-demand system is known as a thermal ink jet or bubble jet printer. The major components are an ink-filled channel with a nozzle at one end and a heat generating resistor near the nozzle. Printing signals create an electric current pulse in a resistive layer within each ink passageway, causing the ink in the immediate vicinity to evaporate, creating a bubble. Some of the ink in the channel is forced out through the orifice as a propelled droplet

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due to bubble expansion. Thermal or bubble ink jet printers produce high velocity droplets and allow very close spacing of nozzles, which results in a high quality of print.

The third type of drop-on-demand ink jet device is known as an acoustic ink printer. This printer utilizes a focused acoustic beam formed with a spherical lens illuminated by a plane wave of sound created by a piezoelectric transducer. The focused acoustic beam exerts pressure on the surface of the liquid, resulting in the ejection of small droplets of ink onto an imaging substrate.

Conventional inks for ink jet printers generally comprise a colorant such as dye which is soluble in a vehicle of water or a mixture comprising water and a water-soluble or water-miscible organic solvent. However, dyes have several disadvantages when used in ink jet inks. Dyes, being water-soluble or soluble in a water and organic mixture, may redissolve and run when exposed to moisture or water. Dye images may smear and rub off on contact with felt pen markers or upon being rubbed with a finger. Dyes also exhibit poor light stability, including fluorescence, sunlight, and ultraviolet light. Inks comprising soluble dyes may also exhibit clogging of the jetting channels due to solvent evaporation and changes in the dye's solubility, dye crystallization, and the presence of impurities. Dye-based ink may also exhibit poor thermal and chemical stability which could result in poor print quality. The dye may also bleed or diffuse into pores of the paper, thus causing poor print quality and low optical density of the image. Specialty paper may be necessary for certain ink jet inks containing a dye. In addition, many of the dyes contained in inks may be potentially mutagenic.

Pigments have also been used as colorants in ink jet inks, either as substitutes for, or in combination with, dyes. Pigments offer properties superior to dyes in areas such as waterfastness, lightfastness, image density, thermal stability, oxidative and chemical stability, compatibility with other colorants, and compatibility with both coated/treated and plain papers. Additionally, pigments are generally nonmutagenic. Pigments used in ink jet inks include carbon black, titanium dioxide white, cobalt blue ($\text{CoO-Al}_2\text{O}_3$), and chrome yellow (PbCrO_4). Carbon black, which absorbs in the infrared region, may be used for bar code reading.

The major problem with the use of such pigments is dispersion. Pigment particles such as carbon black generally start in a clumped or agglomerated state. To prepare ink jet inks, however, the carbon black must be dispersed and stabilized in that form because the extent of dispersion directly affects ink jet printing characteristics such as ejectability, print quality, optical density, and the like. Additionally, since the nozzle openings of thermal or bubble type ink jet printers are typically about 40-60 micrometers in diameter, it is critical to ensure that the ink jet ink does not clog or plug these openings. Thus, it is necessary to make the pigment particles as small as possible. Preferably carbon black is reduced to individual aggregates. Small pigment particles are also less prone to settling during storage and therefore further contribute to the stability of the carbon black dispersion.

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In light of these requirements, conventional aqueous pigment-based ink jet inks generally contain an aqueous ink vehicle, a pigment, a dispersant, and a humectant to prevent drying of ink or the clogging of orifices. Further additives such as biocides, binders, salts, driers, penetrants, surfactants, and the like may also be included.

5 Dispersants are materials that can bind to the pigment with one part of a molecule, while the other is attracted to the vehicle. A dispersant typically coats the pigment particles and then attracts a coating of the vehicle, which allows the coated particles to disperse in the vehicle. Clumping and agglomeration of the pigment particles are therefore minimized due to a steric or electro-steric repulsion caused by the protective coverage.

10 The conventional steps for preparing a pigment-based ink jet ink, as well known in the art, are as follows: First, the pigment must be milled to a small size in the presence of the solvent and the dispersant, by any of a variety of mechanical dispersion processes, including a liquid jet interaction chamber, a media mill, a ball mill, a roll-mill, a speed line mill, a homogenizer, and a sand grinder. Without the milling step, the dispersant will be ineffective. The pigment dispersion
15 may be diluted further with the vehicle to obtain a desired concentration. Finally, some additional ink components, such as humectant, viscosity control additive, biocide, fungicide, pH adjuster, anti-corrosion agent, and the like, may be added to the pigment dispersion. Further dilution with the vehicle may also be made. It may also be necessary to remove larger particles by filtration and/or centrifugation.

20 For general discussion on the properties, preparation, and uses of aqueous inks, see *The Printing Manual*, 5th Ed., Leach et al., Eds. (Chapman & Hall, 1993).

The majority of time and cost is therefore spent on adequately dispersing the pigment in the aqueous medium. The desire to ease and improve dispersion of pigments is reflected in the patents discussed below.

25 U.S. Patent No. 5,184,148 discloses an ink jet ink comprising an aqueous liquid medium containing acid carbon black and a water-soluble resin having a weight average molecular weight within the range of 3,000 to 30,000. The resin acts to improve the dispersion stability of the carbon black in the liquid medium. Other additives such as surfactants, defoaming agents, preservatives, dyes, and the like, may also be included.

30 U.S. Patent No. 4,597,794 discloses an ink jet recording process which uses an ink prepared by dispersing fine particles of a pigment into an aqueous dispersion vehicle containing a polymer having both a hydrophilic and a hydrophobic construction portion. The hydrophilic portion constitutes a polymer of monomers having mainly polymerizable vinyl groups into which hydrophilic portions such as carboxylic acid groups, sulfonic acid groups, and sulfate groups have
35 been included. Examples of the monomers to which hydrophilic groups are attached include styrene and its derivatives, vinyl naphthalene and its derivatives, and α,β -ethylenic unsaturated

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carboxylate of a C₈-C₁₈ aliphatic alcohol. The hydrophobic portion of the polymer adsorbs to the pigment and the hydrophilic portion faces out from the pigment to bond with water or another aqueous solvent. This mechanism produces improved dispersion of the pigment. The ink compositions disclosed may also include additives such as surfactants, salts, resins, and dyes.

5 U.S. Patent No. 4,530,961 discloses an aqueous dispersion of carbon black grafted with hydrophilic monomers of alkali or ammonium carboxylate bearing polyacrylates, which may be used for manufacturing ink jet inks. The carbon black is treated in water with a water-soluble peroxide, and after peroxidation, a water-soluble acrylic monomer and more peroxide are added. This process results in simultaneous homogeneous free radical polymerization of the monomer and
10 grafting onto the carbon black. This composition may also contain surfactants, wetting agents, dyes, or other additives.

U.S. Patent No. 5,281,261 discloses an ink containing carbon black particles having a polymeric vinyl aromatic salt either chemically grafted or adsorbed onto their surfaces. The salt may simply be adsorbed to the surface of the carbon black due to similar hydrophobicity of the
15 carbon black and the aromatic groups of the salt. If the salt is grafted to the carbon black, it is not the aromatic portion of the salt which is directly grafted to the carbon black. Instead, a polymerizable olefinic group on the salt interacts with the carbon black to graft the salt thereon. Additionally, as with typical ink jet inks, additives such as surfactants, wetting agents, dyes, and the like, may be present.

20 The above U.S. Patents and article are incorporated herein by reference.

While the use of pigments such as carbon black in ink jet inks represents an alternative to dyes, there remains a need for a pigment that can be stably dispersed in its smallest particulate form without undue processing and cost.

25 SUMMARY OF THE INVENTION

The present invention relates to an aqueous ink jet ink composition comprising an aqueous vehicle and a modified carbon product containing carbon having attached at least one organic group. Carbon, as used herein, is capable of reacting with a diazonium salt to form the above-mentioned modified carbon product. The carbon may be of the crystalline or amorphous
30 type. Examples include, but are not limited to, graphite, carbon black, vitreous carbon, activated charcoal, activated carbon, and mixtures thereof. Finely divided forms of the above are preferred. The organic group comprises a) at least one aromatic group and b) at least one ionic group, at least one ionizable group, or a mixture of an ionic group and an ionizable group. The organic group having an aromatic group is directly attached to the carbon by the aromatic group.

35 The present invention also relates to an aqueous ink jet ink composition comprising an aqueous vehicle and the above-described modified carbon product. The organic group of the

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modified carbon product comprises a) at least one C_1 - C_{12} alkyl group and b) at least one ionic group, at least one ionizable group, or a mixture of an ionic group and an ionizable group. The ink jet inks of this invention offer desirable dispersion stability, jetability, print quality, and image optical density. The present invention additionally relates to an ink jet recording method having the step of applying to a recording medium ink droplets from orifices of an ink jet recording head, wherein the ink jet ink of the present invention is utilized.

The present invention further relates to a method to increase optical density of an aqueous ink jet ink which includes the step of adding or incorporating the modified carbon product of the present invention into the aqueous ink jet ink.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention relates to an aqueous ink jet ink composition comprising an aqueous vehicle and a modified carbon product. In contrast to conventional carbon pigments, the modified carbon products for use in the ink jet ink of the present invention are not difficult to disperse in an aqueous vehicle. The modified carbon products do not necessarily require a conventional milling process, nor are dispersants necessarily needed to attain a usable ink. Preferably, the modified carbon products only require low shear stirring or mixing to readily disperse the pigment in water.

Carbon, as used herein, is capable of reacting with a diazonium salt to form the above-mentioned modified carbon product. The carbon may be of the crystalline or amorphous type. Examples include, but are not limited to, graphite, carbon black, vitreous carbon, activated charcoal, and activated carbon. Finely divided forms of the above are preferred; also, it is possible to utilize mixtures of different carbons. The carbon products may be prepared by reacting carbon as defined above, with a diazonium salt in a liquid reaction medium to attach at least one organic group to the surface of the carbon. Preferred reaction media include water, any medium containing water, and any medium containing alcohol. Water is the most preferred medium. These modified carbon products, wherein the carbon is carbon black, and various methods for their preparation are described in U.S. patent application 08/356,660 entitled "Reaction of Carbon Black with Diazonium Salts, Resultant Carbon Black Products and Their Uses," filed December 15, 1994, and its continuation-in-part application, filed concurrently with this application, both of which are incorporated herein by reference. These modified carbon products, wherein the carbon is not carbon black, and various methods for their preparation are described in patent application serial number 08/356,653 entitled "Reaction of Carbon Materials with Diazonium Salts and Resultant Carbon Products" filed December 15, 1994, also incorporated herein by reference.

To prepare the above modified carbon products, the diazonium salt need only be sufficiently stable to allow reaction with the carbon. Thus, that reaction can be carried out with

5 some diazonium salts otherwise considered to be unstable and subject to decomposition. Some decomposition processes may compete with the reaction between the carbon and the diazonium salt and may reduce the total number of organic groups attached to the carbon. Further, the reaction may be carried out at elevated temperatures where many diazonium salts may be susceptible to decomposition. Elevated temperatures may also advantageously increase the solubility of the diazonium salt in the reaction medium and improve its handling during the process. However, elevated temperatures may result in some loss of the diazonium salt due to other decomposition processes.

10 Carbon black can be reacted with a diazonium salt when present as a dilute, easily stirred, aqueous slurry, or in the presence of the proper amount of water for carbon black pellet formation. If desired, carbon black pellets may be formed utilizing a conventional pelletizing technology. Other carbons can be similarly reacted with the diazonium salt. In addition, when modified carbon products utilizing carbon other than carbon black are used in ink jet inks, the carbon should preferably be ground to a fine particle size before reaction with the diazonium salt to prevent unwanted precipitation in the ink. A preferred set of organic groups which may be attached to the carbon are organic groups substituted with an ionic or an ionizable group as a functional group. An ionizable group is one which is capable of forming an ionic group in the medium of use. The ionic group may be an anionic group or a cationic group and the ionizable group may form an anion or a cation.

20 Ionizable functional groups forming anions include, for example, acidic groups or salts of acidic groups. The organic groups, therefore, include groups derived from organic acids. Preferably, when it contains an ionizable group forming an anion, such an organic group has a) an aromatic group or a C_1 - C_{12} alkyl group and b) at least one acidic group having a pK_a of less than 11, or at least one salt of an acidic group having a pK_a of less than 11, or a mixture of at least one acidic group having a pK_a of less than 11 and at least one salt of an acidic group having a pK_a of less than 11. The pK_a of the acidic group refers to the pK_a of the organic group as a whole, not just the acidic substituent. More preferably, the pK_a is less than 10 and most preferably less than 9. Preferably, the aromatic group or the alkyl group of the organic group is directly attached to the carbon. The aromatic group may be further substituted or unsubstituted, for example, with alkyl groups. The C_1 - C_{12} alkyl group may be branched or unbranched and is preferably ethyl. More preferably, the organic group is a phenyl or a naphthyl group and the acidic group is a sulfonic acid group, a sulfinic acid group, a phosphonic acid group, or a carboxylic acid group. Examples include $-COOH$, $-SO_3H$ and $-PO_3H_2$, $-SO_2NH_2$, $-SO_2NHCOR$, and their salts, for example $-COONa$, $-COOK$, $-COO^-NR_4^+$, $-SO_3Na$, $-HPO_3Na$, $-SO_3^-NR_4^+$, and PO_3Na_2 , where R is an alkyl or phenyl group. Particularly preferred ionizable substituents are $-COOH$ and $-SO_3H$ and their sodium and potassium salts.

Most preferably, the organic group is a substituted or unsubstituted sulfophenyl group or a salt thereof; a substituted or unsubstituted (polysulfo)phenyl group or a salt thereof; a substituted or unsubstituted sulfonaphthyl group or a salt thereof; or a substituted or unsubstituted (polysulfo)naphthyl group or a salt thereof. A preferred substituted sulfophenyl group is hydroxysulfophenyl group or a salt thereof.

Specific organic groups having an ionizable functional group forming an anion are p-sulfophenyl, 4-hydroxy-3-sulfophenyl, and 2-sulfoethyl.

Amines represent examples of ionizable functional groups that form cationic groups and can be attached to the same organic groups as discussed above for the ionizable groups which form anions. For example, amines may be protonated to form ammonium groups in acidic media. Preferably, an organic group having an amine substituent has a pK_b of less than 5. Quaternary ammonium groups ($-NR_3^+$) and quaternary phosphonium groups ($-PR_3^+$) also represent examples of cationic groups and can be attached to the same organic groups as discussed above for the ionizable groups which form anions. Preferably, the organic group contains an aromatic group such as a phenyl or a naphthyl group and a quaternary ammonium or a quaternary phosphonium group. The aromatic group is preferably directly attached to the carbon. Quaternized cyclic amines, and quaternized aromatic amines, can also be used as the organic group. Thus, N-substituted pyridinium compounds, such as N-methyl-pyridyl, can be used in this regard. Examples of organic groups include, but are not limited to, $3-C_5H_4N(C_2H_5)^+$, $C_6H_4NC_5H_5^+$, $C_6H_4COCH_2N(CH_3)_3^+$, $C_6H_4COCH_2(NC_5H_5)^+$, $3-C_5H_4N(CH_3)^+$, and $C_6H_4CH_2N(CH_3)_3^+$.

An advantage of the modified carbon products having an attached organic group substituted with an ionic or an ionizable group is that the modified carbon products may have increased water dispersibility relative to the corresponding untreated carbon. In general, water dispersibility of the modified carbon products increases with the number of organic groups attached to the carbon having an ionizable group or the number of ionizable groups attached to a given organic group. Thus, increasing the number of ionizable groups associated with the modified carbon products should increase their water dispersibility and permits control of the water dispersibility to a desired level. It can be noted that the water dispersibility of modified carbon products containing an amine as the organic group attached to the carbon may be increased by acidifying the aqueous vehicle.

Because the water dispersibility of the modified carbon products depends to some extent on charge stabilization, it is preferable that the ionic strength of the aqueous medium be less than 0.1 molar. More preferably, the ionic strength is less than 0.01 molar. It is preferred that the modified carbon product of the present invention contain no by-products or salts.

When water dispersible modified carbon products of the present invention are prepared, it is preferred that the ionic or ionizable groups be ionized in the reaction medium. The resulting

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product dispersion or slurry may be used as is or diluted prior to use. Alternatively, the modified carbon products may be dried by techniques used for conventional carbon blacks. These techniques include, but are not limited to, drying in ovens and rotary kilns. Overdrying, however, may cause a loss in the degree of water dispersibility. In the event that the modified carbon products above do not disperse in the aqueous vehicle as readily as desired, the modified carbon products may be dispersed using conventionally known techniques such as milling or grinding.

Formation of an ink jet ink containing an aqueous vehicle and stably dispersed modified carbon product as pigment can be performed with a minimum of components and processing steps when the above carbon products are utilized. Such an ink may be used in any ink jet printer known in the art. Preferably, in ink jet inks of the present invention, the carbon products are present in an amount of less than or equal to 20% by weight of the ink jet ink. It is also within the bounds of the present invention to use an ink jet ink formulation containing a mixture of unmodified carbon with the modified carbon products of the present invention. Common additives such as those discussed below may be added to the dispersion to further improve the properties of the ink jet ink.

In particular, a humectant may be added to reduce the rate of evaporation of water in the ink to minimize clogging. If the ink begins to dry out, the humectant concentration increases and evaporation decreases further. Humectants may also affect other properties of the ink and prints made therefrom, such as viscosity, pH, surface tension, optical density, and print quality. Preferred humectants include ethylene glycol, propylene glycol, diethylene glycols, glycerine, dipropylene glycols, polyethylene glycols, polypropylene glycols, amides, ethers, carboxylic acids, esters, alcohols, organosulfides, organosulfoxides, sulfones, alcohol derivatives, carbitol, butyl carbitol, cellosolve, ether derivatives, amino alcohols, and ketones.

Biocides such as benzoate or sorbate salts are important in preventing bacterial growth. Bacteria are often larger than ink nozzles and can cause clogging and other problems. Binders attach to the substrate to hold the colorant on the paper. Examples include polyester, polyester-melanine, styrene-acrylic acid copolymers, styrene-acrylic acid-alkyl acrylate copolymers, styrene-maleic acid copolymers, styrene-maleic acid-alkyl acrylate copolymers, styrene-methacrylic acid copolymers, styrene-methacrylic acid-alkyl acrylate copolymers, styrene-maleic half ester copolymers, vinyl naphthalene-acrylic acid copolymers, vinyl naphthalene-maleic acid copolymers, and salts thereof. Drying accelerating agents promote evaporation of the ink once the ink is placed on the paper. These include sodium lauryl sulfate, N,N-diethyl-m-tolamide, cyclohexylpyrrolidinone, and butyl carbitol. Penetrants such as alcohols, sodium lauryl sulfate, esters, and ketones allow the ink to penetrate the surface of the paper. Alcohols may also be used to increase the rate of drying of the liquid ink. And surfactants like detergents and soap reduce the surface tension to allow the ink to spread on the substrate.

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Additionally, the modified carbon products-based ink jet inks may incorporate some dye to modify color balance and adjust optical density. Such dyes include food dyes, FD & C dyes, derivatives of phthalocyanine tetrasulfonic acids, including copper phthalocyanine derivatives, tetra sodium salts, tetra ammonium salts, tetra potassium salts, tetra lithium salts, and the like.

5 Polymers or oligomers may be added to ink jet inks based on the modified carbon products. The images created from such an ink may be water-insoluble upon polymerization or cross-linking of the added polymers or oligomers.

10 Additionally, in preparing ink jet inks utilizing the modified carbon product of the present invention, sequential filtration of the inks through filters of descending size may be used to obtain a more desirable final product. For instance, filtering first with a 3.0 micron filter and then filtering with a 1.0 micron filter, and so on, as desired. In addition, the size of the modified carbon product in the ink jet inks is preferably no larger than about 2 microns. More preferably, the size of the modified carbon product is one micron or less.

15 Advantageously, the ink jet inks of the invention have excellent stability over time and a wide range of temperatures, have desirable viscosities and surface tensions, and when printed, have good optical density, print clarity, rub resistance, and waterfastness. Particularly good waterfastness can be obtained when the ink jet ink contains certain styrenated acrylics that impart this property. For instance, one such styrenated acrylic has a molecular weight of about 4200, a polydispersibility of about 2, and acid number of about 215, a softening point of about 128°C, and a T_g of about 67°C. A commercially available example is JONCRYL 58 acrylic (JONCRYL is a registered trademark of Johnson Polymer, Racine WI.), which is a solution of Joncryl 680.

20 With the use of the modified carbon products of the present invention in ink jet ink formulations, a high surface tension of greater than 70 dynes/cm, and a low viscosity of less than 1.9 cP, can be achieved. The surface tension may be lowered, if desired, by the addition of the other ingredients. This flexibility in formulation allows the control of the drop size and uniformity. As reflected in more detail in the Examples below, excellent optical density using the ink jet ink formulations of the present invention was achieved.

The following examples are intended to illustrate, not limit, the claimed invention.

30 Examples:

Procedures Used To Determine Carbon and Ink Properties:

Surface Area:

35 BET nitrogen surface areas obtained according to ASTM D-4820 are used for surface area measurements. CTAB areas were obtained according to ASTM D-3765. DBPA data were obtained according to ASTM D-2414.

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Surface Tension:

The surface tensions of the inks were measured using a CSC-DU NOUY Tensiometer, No. 70535 from CSC Scientific Co., Inc. Fairfax, VA, using the ASTM D 1331 and D 1590 procedures.

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Viscosity:

The ink viscosities were measured using a Cannon-Fenske (Reverse-Flow) viscometer, from Cannon Instrument Co., State College, PA, using ASTM procedures D 445 and D 446. A No. 1 shell cup from Norcross Corp., Newton, MA was also used to measure the viscosities of some of the inks using ASTM procedure D 4212. An excellent correlation between results of both procedures was found.

10

Particle Diameter:

The mean particle diameter and largest detectable diameter were measured using a MICROTRAC Ultrafine Particle Analyzer from Leeds & Northrup Co., St. Petersburg, FL. The following conditions were used: non-transparent, non-spherical particles; particle density = 1.86 g/m^3 ; with water as the dispersing liquid. A run time of six minutes was used. (MICROTRAC is a registered trademark of Leeds & Northrup Co.)

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Optical Density:

The optical density of films, prepared by using a 3 mil Bird applicator to apply a liquid ink coating and then air drying the film, was measured using a MACBETH RD918 Densitometer from Macbeth, New Windsor, NY following ANSI procedure CGATS.4-1993. The optical density was determined on Nashua xerographic, white paper, 20 #, uncoated stock from Nashua Corp., Nashua, NH. (MACBETH is a registered trademark of Kollmorgen Instruments Corp.)

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Print Quality:

Print quality is the sharpness of image (or characters) formed by the ink film on a substrate. The sharpness of the image, which includes being "non-fuzzy", "non-feathering", "non-bleeding", and "non-interrupting" of print, was determined by visual observation. Character alignment, skewness, adjacency, spacing, edge regularity, and non-extraneous ink all contribute to print quality. A relative rating scheme of 1 through 6 was established for prints made. In the visual rating scale, 1 represents the best print quality. All inks with ratings of 1 to 6 produce legible print.

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Water-Resistance:

A qualitative test consisted of putting distilled water on the print and then rubbing with a tissue, and then visually observing the change in print quality and the ink on the tissue.

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Example 1**Preparation of a carbon black product**

A solution of 43 g of sulfanilic acid in 2 L of water at about 75° C was added to 202 g of a carbon black having a surface area of 230 m²/g and a DBPA of 70 ml/100g with stirring. The stirring mixture was allowed to cool to room temperature, and 26.2 g of concentrated nitric acid was added. A solution of 20.5 g of NaNO₂ in water was added. 4-Sulfobenzenediazonium hydroxide inner salt is formed, which reacts with the carbon black. The dispersion was stirred until the resulting bubbling stopped. After drying at 70°C, the product was washed with methanol and dried in an oven at 90°C. The product has attached p-C₆H₄SO₃⁻ groups.

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Example 2**Preparation of a carbon black product**

A pin pelletizer was charged with 42.4 g of sulfanilic acid and with 200 g of a carbon black having a CTAB surface area of 350 m²/g and a DBPA of 120 ml/100g. After mixing for 30 seconds, a solution of 17.4 g NaNO₂ in 150 g of boiling water was added and the mixture was pelletized for 45 seconds. 4-Sulfobenzene-diazonium hydroxide inner salt is formed, which reacts with the carbon black. The product, which was then at 35°C was dried in an oven at 120°C. The product had a 325 mesh residue of 0.2 %, compared to 97 % for the unreacted carbon black. The product has attached p-C₆H₄SO₃⁻ groups.

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Example 3**Preparation of a carbon black product**

This example illustrates the preparation of a carbon black product for use in the present invention. Sulfanilic acid (21 g) was dissolved in 1 L of water with warming. The solution was mixed with 100 g of a carbon black having a surface area of 230 m²/g and a DBPA of 70 ml/100g and allowed to cool to room temperature. An aqueous solution of 10 g NaNO₂ was added slowly and the resulting dispersion was stirred for two hours. 4-Sulfobenzenediazonium hydroxide inner salt is formed in situ, which reacts with the carbon black. The product was dried overnight in an oven at 70°C. The product has attached p-C₆H₄SO₃⁻ groups.

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Example 4**Preparation of a carbon black product**

Anthranilic acid (1.58 g) was added to a solution of 5.0 g concentrated HCl in 5.3 g of water at 5°C. A solution of 1.78 g of NaNO₂ in 8.7 g of water at 5°C was added, keeping the temperature below 10°C by stirring in an ice bath. After stirring for 15 minutes, the solution was added to a stirring suspension of 20 g of a carbon black having a surface area of 320 m²/g and a DBPA of 120 ml/100 g. After stirring for 15 minutes, the product was collected by filtration, washed twice with water and dried in an oven at 110°C. The product has attached o-C₆H₄CO₂⁻ groups.

Example 5**Preparation of a carbon black product**

Silver nitrate (1.69 g) was added to a stirring solution of 3.08 g of H₃NC₆H₄N(CH₃)₃Cl in 30 g of water. The precipitate was removed by filtration, and the remaining solution was added to a stirring suspension of 10.0 g of a carbon black having a surface area of 230 m²/g and a DBPA of 70 ml/100g in 70 g of water. Concentrated HCl (2.25 g) was added and then a solution of 0.83 g NaNO₂ in 10 g of water was added. The diazonium salt N₂C₆H₄N(CH₃)₃⁺⁺ is formed *in situ*, which reacts with the carbon black. Bubbles are released. When the bubbling had stopped, the dispersion was dried in an oven at 120°C. The product had a 325 mesh residue of 0.6 %, compared to 94 % for the unreacted carbon black. The product has attached p-C₆H₄N(CH₃)₃⁺ groups.

Example 6**Preparation of a carbon black product**

Sulfanilic acid (43 g) was dissolved in 2 L of water with warming. The solution was mixed with 200 g of a carbon black having a surface area of 230 m²/g and a DBPA of 70 ml/100g and allowed to cool. An aqueous solution of 20.5 g NaNO₂ was added slowly and the resulting dispersion was stirred for one hour. 4-Sulfobenzenediazonium hydroxide inner salt was formed *in situ*, which reacted with the carbon black. The dispersion was filtered through a Whatman #41 filter, and the product was dried in an oven at 70°C. The product has attached p-C₆H₄SO₃⁻ groups. (6958-77) (M900)

Example 7**Preparation of a carbon black product**

A solution of 17.0 g sulfanilamide and 24.7 mL of concentrated HCl in 100 mL of warm water was prepared. The solution was cooled in an ice bath and a solution of 7.49 g NaNO₂ in

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20 mL of water was added over a period of several minutes. After stirring for 20 minutes, half of the diazonium solution was added to a stirring suspension of 50 g of carbon black having a surface area of 230 m²/g and a DBPA of 70 mL/100g in 250 mL of water. Gas evolution is observed after about 5 minutes, and the suspension was stirred for three hours. The carbon black product is recovered by drying the dispersion in an oven at 125°C. The product has attached p-C₆H₄SO₂NH₂ groups.

Example 8

Preparation of an ink jet ink

This example illustrates the preparation of an ink jet ink of the present invention. Sulfanilic acid (4.25 g) was dissolved in hot water and filtered while hot. Twenty five grams of a carbon black having a surface area of 230 m²/g and a DBPA of 70 ml/100g was added, and the stirring mixture was cooled to 30 °C. Concentrated HCl (5.33 g) was added and then 2.03 g of NaNO₂ dissolved in a small amount of water was added over a period of one hour. When bubbling was complete, the carbon black product in the dispersion had attached p-C₆H₄SO₃⁻ groups. Water was then added to dilute the carbon black product concentration to 3 wt. %. The dispersion was subjected to centrifugation for 10 minutes at 1000 rpm and filtered through a 1.2 micron filter. The dispersion was concentrated in an oven until the carbon black product concentration reached 10 wt. %. The dispersion was refiltered through a 1.2 micron filter, and adjusted to pH 9 with the addition of NaOH solution. The median particle size of the carbon black product in the resulting ink jet ink was 0.06 microns. A sample of the ink that was diluted to a 5 wt. % carbon black content had a viscosity of 1.17 cp and a surface tension of 76.5 dynes/cm.

A sample of the ink that had been diluted to a 5 wt. % carbon black content and subjected to three freeze thaw cycles had a viscosity of 1.20 cp, and a surface tension of 76 dynes/cm. The carbon black product in this ink had a median particle size of 0.05 microns.

A sample of the ink that had been diluted to a 5 wt. % carbon black content and that was heated in a sealed container for one week at 70°C had a viscosity of 1.13 cp, and a surface tension of 76 dynes/cm. The carbon black product in this ink had a median particle size of 0.06 microns.

Example 9

Preparation of ink jet inks

Sulfanilic acid (34.3 g) is dissolved in 2L of hot water. Two hundred grams of a carbon black having a surface area of 230 m²/g and a DBPA of 70 ml/100g were added and the mixture was cooled to room temperature. Concentrated nitric acid (21.2 g) was added. A solution of 16.5 g NaNO₂ in 40 g water was added slowly. After stirring, the resulting dispersion, which

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contained a carbon black product having attached $\text{p-C}_6\text{H}_4\text{SO}_3^-$ groups, was filtered through a 1.2 micron filter. This dispersion was useful as an ink jet ink and was stable at room temperature for months. The carbon black product contained in the ink had a median particle size of <0.1 microns.

Addition of an equal volume of a solution of 1.5 % to 3 % polyvinyl alcohol (99% hydrolyzed, MW 13000) in water to the ink jet ink give inks that made prints with improved dry rub resistance. The prints did not bleed when immersed in water for one minute, but they were not fast when rubbed in the wet state.

Examples 10-26

Preparation of ink jet inks

These examples illustrate the preparation of ink jet inks of the present invention. Carbon black products were dispersed in water at the concentrations indicated. The pH was increased to about 9 with the addition of N,N dimethylethanolamine, except in Example 25, where the pH was adjusted to 12 with NaOH. Additives such as humectants, polymers or dyes were then added as indicated. The inks were filtered through a Fisher Q8 paper filter, a Whatman GMF-2 micron filter and then a Whatman GMF-1 micron filter to remove coarse contaminants. Prints were made from these inks with a commercial ink jet printer on xerographic uncoated white paper stock. These results show that a variety of humectants, polymers and dyes can be added to give useful ink jet inks with differing properties. Prints made from inks of Examples 23 and 24 had excellent wet rub resistance properties. Prints made from the ink of Example 25 had good wet rub resistance properties. Prints made from the ink of Example 26 had good wet rub resistance when the print was dried at room temperature and excellent wet rub resistance properties when the prints were dried at 200°C for one minute.

Example	Carbon Black Product of Example	Carbon Black Product Concentration %	Additive	Additive Concentration	ST	Visc (cp)	MD (um)	LD (um)	PQ	OD
10	1	10	-	-	68.5	1.28	0.09	0.41	5	1.17
11	2	5	-	-	74.7	N/A	0.19	0.69	5	1.00
12	1	10	EG	10	71.4	2.11	0.12	0.49	1	1.27
13	3	10	PEG, MW 200	10	67.8	N/A	0.06	0.24	5	1.23
14	3	10	PEG, MW 300	10	66.9	N/A	0.07	0.29	5	1.21
15	1	10	PEG, MW 350	10	71.4	N/A	0.12	0.58	3	1.17
16	3	10	PEG, MW 1000	10	66.5	N/A	0.07	0.24	2	1.23

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Example	Carbon Black Product of Example	Carbon Black Product Concentration %	Additive	Additive Concentration	ST	Visc (cp)	MD (um)	LD (um)	PQ	OD
17	3	10	DEG	10	68.8	N/A	0.06	0.20	2	1.24
18	1	15	2-Propanol	10	42.6	N/A	0.11	0.41	5	1.10
19	4	4	-	-	74.5	1.04	0.27	1.16	6	0.18
20	1	10	DB19	0.7	72.9	1.38	0.11	0.49	3	1.18
21	2	5	DB19	1.0	73.4	1.14	N/A	N/A	4	1.06
22	1	10	ACR	10	48.1	2.29	0.13	0.52	2	0.99
23	5	10	-	-	N/A	N/A	0.10	0.29	4	N/A
24	5	10	EG	10	N/A	N/A	N/A	N/A	5	N/A
25	7	5	-	-	74.4	1.3	0.08	0.41	4	1.21
26	6	10	PE/M/EG/PJB	15/6/5/1	45.8	2.0	0.07	0.41	6	1.27

EG= ethylene glycol

PEG= polyethylene glycol

DEG= diethylene glycol

DB19= direct black 19

ACR= JONCRYL 62 acrylic resin solution. JONCRYL is a registered trademark of Johnson Polymer, Racine WI.

PE= 072-7232 polyester solution, McWhorter Technologies, Chicago Heights, IL

M= 023-2347 Melamine, Cargill Inc, Forest Park, GA

PJB=Projet black 1 dye solution, Zeneca, Wilmington, DE

ST= surface tension (dynes/cm)

MD= mean diameter (um)

LD= largest detectable Diameter (um)

Visc= viscosity (cP)

PQ= Print Quality, Visual Rating

OD= optical density (Macbeth reflection densiometer)

Example 27**Preparation of treated carbon black products and ink jet inks**

This example illustrates the preparation of several carbon black products and the preparation of ink jet inks from them. Fifteen carbon blacks were used as shown below. In each case, sulfanilic acid was dissolved in about 90 g of water. In some cases heat was required to complete the dissolution. Ten grams of carbon black was added and the mixture was stirred well. A 10% solution of sodium nitrite in water was added over a few minutes. In all cases, the sulfanilic acid addition level was 0.91 mg/m² and the sodium nitrite addition level was 0.40 mg/m². Gas evolution was observed and the dispersion was stirred for about 20 minutes. The carbon black product was recovered by drying the dispersion in an oven at 70 °C. The carbon black products had attached p-C₆H₄SO₃⁻ groups.

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Ink jet inks were prepared by stirring the carbon black products with water to make dispersions with a 5 % solids content. Drawdowns of the inks were made with a BYK- Gardner automatic drawdown device using a 3 mil bar applicator on Nashua 20 lb. dual purpose uncoated paper. The optical densities were measured and are shown below. These results show that the optical density of prints made from the inks depend on the carbon black used in preparation of the carbon black product in the ink.

Carbon black surface area, m ² /g	Carbon black DBPA mL/100g	Print optical density
560*	90	1.24
560*	100	1.24
240	65	1.21
343*	110	1.42
230	70	1.3
220	112	1.42
210	74	1.33
200	122	1.55
140	116	1.57
140	114	1.45
112	65	1.27
110	114	1.49
96*	71	1.26
94	65	1.28

* Samples that have been oxidized

Example 28

Preparation of a treated carbon black product and ink jet inks

This example illustrates the preparation of a carbon black product and the preparation of ink jet inks from it. A carbon black with a surface area of 140 m²/g and a DBPA of 114 mL/100g was used. A solution of 1.3 g of sulfanilic acid in about 90 g of water was prepared. Ten grams of

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carbon black was added and the mixture was stirred well. A solution of 0.56 g of sodium nitrite in about 5 g of water was added over a few minutes. Gas evolution was observed and the dispersion was stirred for about 20 minutes. The carbon black product was recovered by drying the dispersion in an oven at 70 °C. The carbon black product had attached $p\text{-C}_6\text{H}_4\text{SO}_3^-$ groups.

Ink jet inks were prepared by stirring the carbon black product with water to make dispersions with solids contents from 0.5 to 15%. Drawdowns of the inks were made with a BYK- Gardner automatic drawdown device using a 3 mil bar applicator on Nashua 20 lb. dual purpose uncoated paper. The optical densities were measured and are shown below. These results show that the optical density of prints made from the inks depends on the concentration of the carbon black product in the ink.

Solids Content, %	Optical Density
0.5	0.56
1	0.74
2	1.16
3	1.28
4	1.44
5	1.50
6	1.56
8	1.61
10	1.65
12	1.68
15	1.73

Example 29

Preparation of a carbon black product

Ten grams of a carbon black with a surface area of 230 m²/g and a DBPA of 70 m²/g was added to a stirring solution of 3.06 g of 3-amino-N-ethylpyridinium bromide in 72 g of water. Concentrated nitric acid (1.62 g) was added, and the mixture was stirred and heated to about 70 °C. A solution of 1.07 g NaNO₂ in about 5g of water was added over a few minutes. The diazonium salt $\text{N}_2\text{C}_5\text{H}_4\text{N}(\text{C}_2\text{H}_5)^{++}$ was formed in situ, which reacted with the carbon black. After the reaction mixture was stirred for one hour, the sample was dried in an oven at 125 °C.

The product had a mean volume particle size of 0.18 microns. The product had attached $3\text{-C}_6\text{H}_4\text{N}(\text{C}_7\text{H}_5)^+$ groups.

Example 30

Preparation of a carbon black product

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Example 31

Preparation of a carbon black product

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Example 32**Preparation of a carbon black product**

Silver nitrite (30.9g) was added to a solution of 41.4 g of N-(4-aminophenyl)pyridinium chloride in 700 g of water and the mixture was stirred at 70 °C for 1 1/2 hours. The mixture was filtered and 200 g of a carbon black with a surface area of 200 m²/g and a DBPA of 122 mL/100 g was added. An additional one liter of water and 20 g of concentrated HCl were added. The diazonium salt N₂C₆H₄NC₅H₅⁺⁺ was formed in situ, which reacted with the carbon black. Bubbles were released. The dispersion was stirred at 70-80°C for 2 1/2 hours and then dried in an oven at 125 °C. The product had attached C₆H₄NC₅H₅⁺ groups.

Example 33**Preparation of a carbon black product**

A pin pelletizer was charged with 41.2 g of 4-aminobenzoic acid and 300 g of a carbon black with a surface area of 200 m²/g and a DBPA of 122 mL/100g. After mixing thoroughly, 100 g water, a solution of 20.7 g NaNO₂ in 50 g of water and then 100 g of water were added while the pelletizer was running. A diazonium salt was formed in situ, which reacted with the carbon black. After mixing an additional four minutes, the sample was removed. The product had attached C₆H₄CO₂⁻ groups.

Example 34**Preparation of a carbon black product**

In a modification of a procedure from US Patent 2,821,526, a mixture of 250 g p-acetaminophenacyl chloride, 65 g of trimethylamine and about 600 g of water was stirred for three days at room temperature. An additional 5 g of trimethylamine in 15 g water was added and the mixture was heated at 60 °C for two hours. After cooling and filtering, 201 g concentrated HCl was added and the solution was boiled for an hour. After cooling, 4L of acetone was added and 4-aminophenacyltrimethylammonium chloride hydrochloride was collected as a solid. 4-Aminophenacyltrimethylammonium chloride hydrochloride (10.1 g) was suspended in 50 mL of ethanol. After addition of 4.1 g triethylamine, the mixture was stirred for 40 minutes and heated at reflux for one hour. 4-Aminophenacyl-trimethylammonium chloride was collected by filtration and washed with ethanol.

4-Aminophenacyltrimethylammonium chloride (2.51 g) was dissolved in water. Silver nitrite (1.69 g) was added, and the mixture was heated at 70 °C for one hour. After filtering off the precipitate, 10 g of a carbon black with a surface area of 230 m²/g and a DBPA of 70 mL/100g was added. Water was added to bring the volume up to about 100 mL. Concentrated HCl (1.1g) was added and the dispersion was heated with stirring at 70 °C for one hour. The diazonium salt

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$\text{N}_2\text{C}_6\text{H}_4\text{COCH}_2\text{N}(\text{CH}_3)_3^{++}$ was formed in situ, which reacted with the carbon black. Bubbles were released. The product had attached $\text{C}_6\text{H}_4\text{COCH}_2\text{N}(\text{CH}_3)_3^+$ groups.

Example 35

Preparation of a carbon black product

A solution of 2.12 g of 4-acetaminophenacyl chloride, 0.83 g of pyridine and 6.4 g of dimethylsulfoxide was stirred overnight. After addition of an additional 0.8 g of pyridine and 1 g of dimethylsulfoxide, the solution was stirred an additional 5 hours. Ether (50 mL) was added, and acetamidophenacylpyridinium chloride was collected by filtration. The acetamidophenacylpyridinium chloride was dissolved in water, the solution filtered and 1.7 g concentrated HCl was added. After boiling for one hour, the solution was cooled, acetone was added, and 4-aminophenacylpyridinium chloride hydrochloride was collected by filtration. Two grams of 4-aminophenacylpyridinium chloride hydrochloride was dissolved in 15 g water and 4.5 g of a basic ion exchange resin (Amberlite IRA400-OH) was added. After stirring, the resin was removed by filtration and 4-aminophenacylpyridinium chloride was collected as an aqueous solution.

A solution of 1.3 g of 4-aminophenacylpyridinium chloride in 25 g of water was heated at reflux with 1 g silver nitrite for about 90 minutes. The precipitate was removed by filtration. Five grams of a carbon black with a surface area of $200 \text{ m}^2/\text{g}$ and a DBPA of 122 mL/100g were added and the mixture was heated to about 80°C . Concentrated HCl (0.52 g) was added and the dispersion was stirred an additional 1 1/2 hours. The diazonium salt $\text{N}_2\text{C}_6\text{H}_4\text{COCH}_2(\text{NC}_5\text{H}_5)^{++}$ was formed in situ, which reacted with the carbon black. The product had attached $\text{C}_6\text{H}_4\text{COCH}_2(\text{NC}_5\text{H}_5)^+$ groups.

Example 36

Preparation of ink jet inks

The carbon black products shown below were stirred into water at a 10% solids content. The samples were centrifuged, the supernatant was decanted and replaced with distilled water to give the ink jet inks. Drawdowns of the inks were made with a BYK- Gardner automatic drawdown device using a 3 mil bar applicator on Nashua 20 lb. dual purpose uncoated paper. After the drawdowns had dried for about half an hour, the optical densities of the prints were measured. The drawdowns were washed with 20 mL of water in a small stream. After drying, the optical densities were measured again. These results show that the ink jet inks of the present invention can produce optically dense prints with good waterfastness.

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Carbon black product	Median particle size, μm	Initial optical density	Optical density after washing
Example 29	0.26	1.27	1.31
Example 30	0.17	1.19	1.19
Example 31	0.24	1.25	1.29

Example 37**Preparation of ink jet inks**

Ink jet inks were prepared by stirring carbon black products into water at the concentrations indicated below. Drawdowns of the inks were made with a BYK- Gardner automatic drawdown device using a 3 mil bar applicator on Nashua 20 lb. dual purpose uncoated paper. After the drawdowns had dried for the indicated time, the optical densities of the prints were measured. The drawdowns were washed with a stream of water until any ink stopped washing off. After drying, the optical densities were measured again. These results show that the ink jet inks of the present invention can produce optically dense prints with good waterfastness.

Carbon black product	Concentration	Median particle size, μm	Dry time	Initial optical density	Optical density after washing
Example 32	10%	0.34	0.5 Hr	1.55	1.40
Example 32	5%	0.34	0.5 Hr	1.32	1.25
Example 32	5%	0.34	4 Days	1.32	1.30
Example 33	5%	0.22	0.5 Hr	1.53	1.49
Example 34	5%	0.07	0.5 Hr	1.01	0.70
Example 35	6%	0.94	0.5 Hr	1.23	1.23

Example 38**Preparation of a carbon black product and ink jet inks**

A mixture of 4.8 g of sulfanilic acid, 40 g of a carbon black with a surface area of $200 \text{ m}^2/\text{g}$ and a DBPA of 122 mL/100g and 400 g of water was stirred. A solution of 1.91 g NaNO_2 in 20 g of water was added and the mixture was stirred for one hour.

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Ink jet inks were prepared by mixing the dispersion of the carbon black product with water and other ingredients as shown below so the concentration of the carbon black product was 7%. The pH of all samples was adjusted to 8.5 with the addition of N.N-dimethylethanolamine.

Drawdowns of the inks were made with a BYK-Gardner automatic drawdown device using a 3 mil bar applicator on Nashua 20 lb. dual purpose uncoated paper. After the drawdowns had dried for the indicated time, the optical densities of the prints were measured. The drawdowns were washed with a stream of water until any ink stopped washing off. After drying, the optical densities were measured again.

Added material	Original optical density	Optical density after washing
None	1.21	1.00
10% Ethylene glycol	1.26	0.96
10% Diethylene glycol	1.31	0.94
6% Joncryl 58	1.41	1.43
10% Ethylene glycol 6% Joncryl 58	1.38	1.45
10% Diethylene glycol 6% Joncryl 58	1.45	1.38

Joncryl 58 is a trademarked styrenated acrylic resin solution of Johnson Polymer, Racine, WI.

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What is claimed is:

1. An aqueous ink jet ink composition comprising an aqueous vehicle and a modified carbon product comprising carbon having attached at least one organic group, the organic group comprising a) at least one aromatic group, and b) at least one ionic group, at least one ionizable group, or a mixture of an ionic group and an ionizable group, wherein the at least one aromatic group of the organic group is directly attached to the carbon.
2. The composition of claim 1 wherein the modified carbon product is present in an amount of less than or equal to 20% by weight of the ink jet ink.
3. The composition of claim 1 wherein the aqueous vehicle is water.
4. The composition of claim 1 wherein the aqueous vehicle is water and a water-miscible solvent.
5. The composition of claim 1 further comprising a humectant.
6. The composition of claim 5 wherein the humectant is at least one compound selected from the group consisting of ethylene glycol, diethylene glycol, propylene glycol, glycerine, dipropylene glycols, polyethylene glycols, polypropylene glycols, amides, ethers, carboxylic acids, esters, alcohols, organosulfides, organosulfoxides, sulfones, alcohol derivatives, carbitol, butyl carbitol, cellosolve, ether derivatives, amino alcohols, and ketones.
7. The composition of claim 1 further comprising a binder.
8. The composition of claim 1 further comprising a dye.
9. The composition of claim 1 further comprising at least two additives selected from the group consisting of humectants, binders, dyes, biocides, penetrants, and surfactants.
10. The composition of claim 1 wherein the ionic or the ionizable group is a carboxylic acid or a salt thereof.
11. The composition of claim 1 wherein the ionic or the ionizable group is a sulfonic acid or a salt thereof.
12. The composition of claim 1 wherein the organic group is a sulfophenyl group or a salt thereof.
13. The composition of claim 1 wherein the organic group is p-sulfophenyl or a salt thereof.
14. The composition of claim 1 wherein the organic group is p-C₆H₄SO₃Na.
15. The composition of claim 1 wherein the organic group is a carboxyphenyl group or a salt thereof.
16. The composition of claim 1 wherein the ionic or the ionizable group is a quaternary ammonium salt.
17. The composition of claim 1 wherein the ionic or the ionizable group is a sulfonamide or a salt thereof.

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16. The composition of claim 1 wherein the ionic or the ionizable group has the formula -
SO₂NHCOR or a salt thereof, where R is a C₁-C₂₀ alkyl or a phenyl group.
19. The composition of claim 1 where the organic group has the formula p-C₆H₄SO₂NH₂.
20. The composition of claim 1 wherein the carbon is carbon black, graphite, vitreous
5 carbon, finely-divided carbon, activated charcoal, activated carbon, or mixtures thereof.
21. The composition of claim 20, wherein the carbon is carbon black.
22. An aqueous ink jet ink composition comprising an aqueous vehicle and a modified
carbon product comprising carbon having attached at least one organic group, the organic group
comprising a) at least one C₁-C₁₂ alkyl group, and b) at least one ionic group, at least one
10 ionizable group, or a mixture of an ionic group and an ionizable group, wherein the at least one
alkyl group of the organic group is directly attached to the carbon.
23. The composition of claim 22 wherein the ionic or the ionizable group is an ethane
sulfonic acid or a salt thereof.
24. The composition of claim 22 further comprising at least two additives selected from
15 the group consisting of humectants, binders, dyes, biocides, penetrants, and surfactants.
25. The composition of claim 22, wherein the carbon is carbon black, graphite, finely-
divided carbon, vitreous carbon, activated carbon, activated charcoal, or mixtures thereof.
26. The composition of claim 25, wherein the carbon is carbon black.
27. An ink jet recording method, comprising the step of:
20 applying to a recording medium ink droplets discharged from orifices of an ink jet recording
head, wherein said ink comprises an aqueous vehicle and a modified carbon product comprising
carbon having attached at least one organic group, the organic group comprising a) at least one
aromatic group, and b) at least one ionic group, at least one ionizable group, or a mixture of an
ionic group and an ionizable group, wherein the at least one aromatic group of the organic group
25 is directly attached to the carbon.
28. The method of claim 27, wherein the ink further comprises at least two additives
selected from the group consisting of humectants, binders, dyes, biocides, penetrants, and
surfactants.
29. The composition of claim 27, wherein the carbon is carbon black, graphite, finely-
30 divided carbon, vitreous carbon, activated carbon, activated charcoal, or mixtures thereof.
30. An ink jet recording method, comprising the step of:
applying to a recording medium ink droplets discharged from orifices of an ink jet recording
head, wherein said ink comprises an aqueous vehicle and a modified carbon product comprising
carbon having attached at least one organic group, the organic group comprising a) at least one
35 C₁-C₁₂ alkyl group, and b) at least one ionic group, at least one ionizable group, or a mixture of

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an ionic group and an ionizable group, wherein the at least one alkyl group of the organic group is directly attached to the carbon.

31. The method of claim 30, wherein the ink further comprises at least two additives selected from the group consisting of humectants, binders, dyes, biocides, penetrants, and surfactants.

32. The composition of claim 30, wherein the carbon is carbon black, graphite, finely-divided carbon, vitreous carbon, activated carbon, activated charcoal, or mixtures thereof.

33. A method for increasing the optical density of an aqueous ink jet ink, comprising the step of:

incorporating into the aqueous ink jet ink a modified carbon product comprising carbon having attached at least one organic group, the organic group comprising a) at least one aromatic group, and b) at least one ionic group, at least one ionizable group, or a mixture of an ionic group and an ionizable group, wherein the at least one aromatic group of the organic group is directly attached to the carbon.

34. A method for increasing the optical density of an aqueous ink jet ink, comprising the step of:

incorporating into the aqueous ink jet ink a modified carbon product comprising carbon having attached at least one organic group, the organic group comprising a) at least one C_1 - C_{12} alkyl group, and b) at least one ionic group, at least one ionizable group, or a mixture of an ionic group and an ionizable group, wherein the at least one alkyl group of the organic group is directly attached to the carbon.

35. The composition of claim 16, wherein said organic group is $3-C_5H_4N(C_2H_5)^+$, $C_6H_4NC_5H_5^+$, $C_6H_4COCH_2N(CH_3)_3^+$, $C_6H_4COCH_2(NC_5H_5)^+$, $C_6H_4CH_2N(CH_3)_3^+$ or $3-C_5H_4N(CH_3)^+$.

36. The aqueous ink jet composition of claim 1, wherein said modified carbon product has a size less than or equal to one micron.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/16195

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D11/00 C09C1/56

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09D C09C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,92 13983 (CNRS) 20 August 1992 see claim 20	1
A	--- DATABASE WPI Week 8002 Derwent Publications Ltd., London, GB; AN 80-03330C & SU,A,659 523 (POLYGRAPHY PROBLEMS) , 30 April 1979 see abstract	1
A	--- DATABASE WPI Week 9423 Derwent Publications Ltd., London, GB; AN 94-189154 & JP,A,06 128 517 (NIPPON SHOKUBAI) , 10 May 1994 see abstract	1

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

9 April 1996

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19.04.96

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